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TEMPERATURE EFFECTS IN THIXOTROPIC SYSTEMS¹

BY G. B. MOSES, A. F. SIRIANNI, AND I. E. PUDDINGTON

ABSTRACT

The effect of temperature and high shear on the coefficients of thixotropy of some grease-like systems has been examined. A temperature dependent interparticle bonding that is destroyed for long periods of time by high shear, particularly in the case of sodium soaps, is observed. This is apparently a sintering phenomenon as recovery can be induced by heating to a specific temperature. Reduced temperature dependence in the thixotropy of nonsoap pastes has been observed although this is considerably modified if the nature of the surface of the solid particles is altered.

TEMPERATURE EFFECTS IN THIXOTROPIC SYSTEMS

Earlier publications (3, 4) dealing with the rheological properties of dispersions of soaps in hydrocarbon oils have shown a dependence of the coefficients of thixotropy of the systems on temperature. This was more pronounced with systems containing sodium and lithium than with other metallic soaps. It was also shown that violent shearing at room temperature, such as passing the paste through a colloid mill, reduced this effect, particularly in the case of the sodium soap systems. In the light of existing data this appeared to be due to a reduction in the fiber length of the soap particles as they passed through the mill, thus making mechanical entanglements less frequent and more easily pulled apart with shear. Further experimental work on this subject, however, has failed to support this conclusion and has indicated a different sort of interparticle adhesion than would be expected from mechanical entanglements or interfacial surface tension.

Should the mechanism suggested previously be valid, a sodium soap grease that contained very short fibers or spherical particles should show a very small temperature dependence of the coefficient of thixotropy. A grease of this kind was prepared by mixing together appropriate amounts of a dispersion of finely divided sodium hydroxide in an oil of 300 S.U.S. visc. and 43 V.I. with a warm solution of stearic acid in the same oil. Saponification was fast and considerable heat evolved. For a grease that contains 10% of soap the temperature rise due to the reaction is about 15° C. The product formed was non-fibrous as indicated by microscopic examination.

¹ Manuscript received January 16, 1953.

Contribution from the Division of Applied Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 2964.

The thixotropic behavior of this grease is indicated in Fig. 1. This is virtually identical with that of a 15% dispersion of sodium stearate in a similar oil prepared in the conventional way. When a small excess of stearic acid (0.1%) is present, the initial value of θ is higher and the fall with increasing temperature, greater. Exposing these fiberless greases to high shear at room temperature greatly reduces this large change in thixotropy with increasing temperature. Since shear under these conditions should not affect the ultimate soap particles to a great extent, the large change in thixotropy cannot be due to particle shape alone. Furthermore, when the axial ratio of the particles of soap in the fiberless grease was considerably increased by shearing the system at a temperature of about 120° C. (1), the degree of thixotropy was actually reduced as shown in Fig. 1.

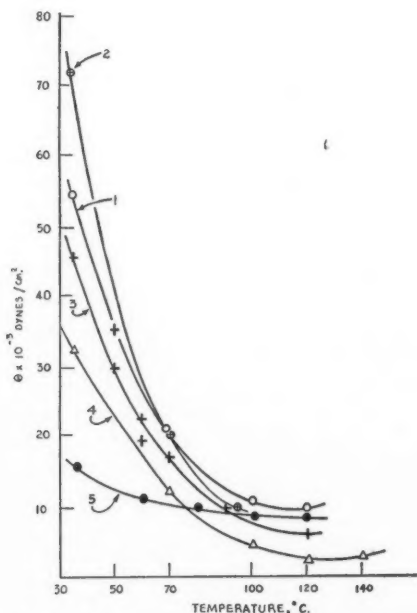


FIG. 1. Changes in the coefficients of thixotropy of soap-oil systems with temperature. Curve 1, 10% of neutral sodium stearate in 300 visc. 45 V.I. oil. Curve 2, 10% of sodium stearate containing 0.1% of free stearic acid in oil. Curve 3, conventional grease containing 15% of sodium stearate. Curve 4, sample used for Curve 1 after high shear at 120° C. Curve 5, sample used for Curve 1 after high shear at room temperature.

Since the large dependence of thixotropy on temperature does not appear to be connected with fiber length, the possibility of this being due to interparticle sintering was examined. Such an explanation would not be inconsistent with the experimental observations provided that the strength of the interparticle bonds decreased with rise in temperature. To investigate this point a commercial grease containing 14% of sodium stearate in 300 visc.

45 V.I. oil (4) was highly sheared by passage twice through a colloid mill at room temperature and the coefficient of thixotropy at 35° C. was determined in the usual way. The grease was then heated to progressively higher temperatures for one hour. After each new temperature, the system was cooled to 35° C. and the coefficient of thixotropy redetermined. The results of this examination are shown in Fig. 2.

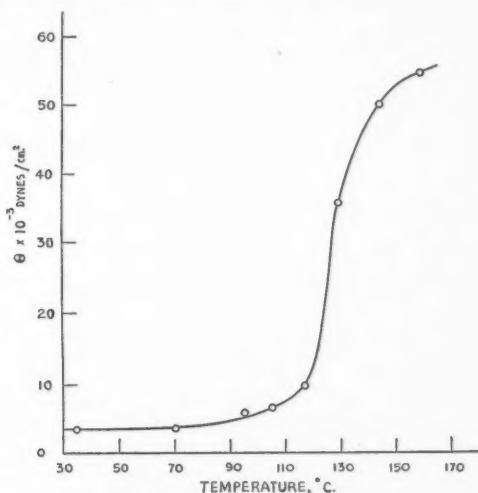


FIG. 2. Changes in coefficient of thixotropy at 35° C. for a grease containing 14% of sodium stearate that has been highly sheared at room temperature and then heated to progressively higher temperatures.

Apparently there is little change in interparticle bonding until the temperature is reached at which the soap begins to imbibe oil—a temperature that corresponds to a phase change involving a large density difference in the soap. Heating the grease to intermediate temperatures regardless of the degree of breakdown has little effect during the times involved here, although there is a qualitative evidence that partial thixotropic recovery takes place at low temperatures over a period of days or weeks. The rise of 15° C. in the over-all temperature of the system during an *in situ* saponification of a 10% soap dispersion is ample to raise the temperature of the individual soap particles to temperatures sufficiently high to produce adhesion and cause the initially high thixotropy, if one assumes similar values for the specific heat of oil and soap and a low thermal loss from the soap particles during the very fast saponification reaction.

It would therefore appear that an important factor in the agglomeration of sodium soap particles in oil is a form of sintering and that the sintered bond strength is temperature dependent. This probably accounts for the large difference in the worked and unworked penetration of normal sodium soap lubricants. The practice of shearing in the cold that is used occasionally to

lessen the gap in the worked and unworked penetration is open to question if these greases are to be exposed to temperatures in excess of about 100° C. since the soap particles should then sinter and produce a very heavy-bodied lubricant when the system is again cooled. The temperature to which the system may be safely heated varies somewhat with the fatty acids contained in the sodium soaps.

Experiments similar to the above were carried out on systems containing calcium and lithium soaps instead of sodium. The variation of thixotropy with temperature in calcium soap base greases is almost independent of the amount of shear to which the system has been subjected. With lithium soaps the effect was comparatively small and no recovery could be detected after heating, indicating that the small effect was due mainly to mechanical breaking of the soap particles.

In view of these results with soap-oil systems, it is of interest to investigate the effect of temperature and shear on the flow properties of thixotropic oil base systems wherein the soap has been replaced by other solid materials. Several of these have been prepared in considering possible substitutes for soaps in greases.

Pastes of silica and oil are easily produced by agitating an appropriate mixture of finely divided silica and oil at room temperature. The silica disperses equally well in oils of all viscosity index in contrast to the behavior of soaps under similar circumstances, and the volume concentration of the solid phase necessary to produce a paste of given rigidity is about one-half to one-third of that required when soap is used. Another inorganic material that gives pastes with similar properties is a form of bentonite that has been chemically treated to give it swelling properties in nonaqueous media (2). It is somewhat selective in its compatibility with oil and frequently requires heating to give a desirable dispersion. Grease-like pastes may also be obtained by incorporating Shawinigan black, a very finely divided form of carbon, into lubricating oils. Since the state of subdivision of these solids is of the same order as the soap in greases and none of them exhibit phase transitions on heating to temperatures normally encountered in lubrication, the flow properties of pastes prepared from them are of considerable interest.

The finely divided carbon black was discarded after a preliminary examination since examination indicated that, although a grease-like material was formed when the carbon was initially incorporated into the oil, the apparent viscosity decreased greatly with shear and the recovery was extremely slow. Furthermore, small increments in the concentration of carbon black caused rather large increases in the residual viscosity of the system, without producing the very large increases in thixotropy that are required for greases. This result is not unexpected in view of the hydrocarbon nature of the surface of the carbon black and the fact that it is apparently in a highly agglomerated state prior to its incorporation into the oil.

Results with the siliceous materials are of considerable interest and these are shown in Figs. 3 and 4. The silica used was in the aerogel form. Laboratory-

prepared samples were washed free of electrolytes prior to preparing the aerogel while commercial samples probably contained some sodium sulphate (about 3-5%). With oils of medium viscosity, 300-500 S.U.S. at 100° F., the temperature coefficient of thixotropy was very small. This is in contrast to the behavior of soap-oil systems and represents a very desirable type of flow

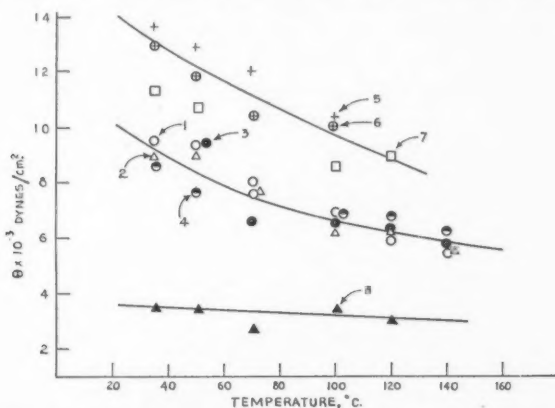


FIG. 3. Changes in the coefficients of thixotropy of silica-oil systems with temperature. Curve 1, 8% by weight of commercial silica aerogel in 300 visc. 95 V.I. oil; Curve 2, as Curve 1 with 500 visc. 95 V.I. oil; Curve 3, as Curve 1 with 900 visc. 95 V.I. oil; Curve 4, as Curve 1 with 300 visc. 45 V.I. oil; Curve 5, 8% by weight of laboratory-prepared silica aerogel in 300 visc. 95 V.I. oil; Curve 6, as Curve 5 but 2% of water added; Curve 7, as Curve 5 with 0.2% of water added; Curve 8, as Curve 5 but with 5% by weight of laboratory-prepared silica aerogel.

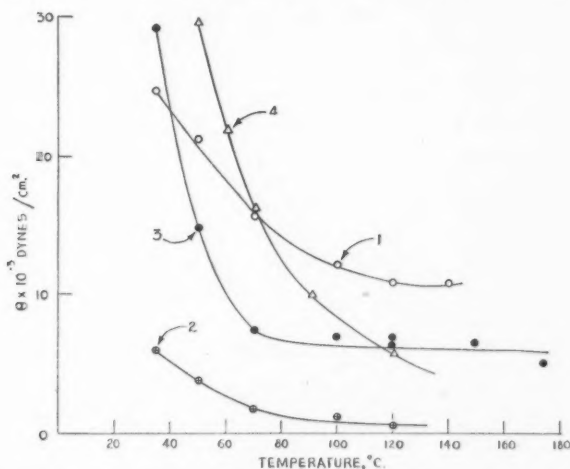


FIG. 4. Changes in the coefficients of thixotropy of coated silica-oil systems. Curve 1, 10% by weight of alkyl coated commercial silica aerogel in 300 visc. 95 V.I. oil; Curve 2, 8% of hydrocarbon coated commercial silica aerogel in 300 visc. 95 V.I. oil; Curve 3, 12% of Bentone 34 in 300 visc. 45 V.I. oil; Curve 4, 15% of sodium stearate in 300 visc. 45 V.I. oil.

from the lubrication standpoint. When the viscosity of the oil phase is markedly increased, either by cooling the system or by using an oil of higher original viscosity, the coefficient of thixotropy shows a marked increase. This increase starts to appear when the oil viscosity reaches a value of about 1500 S.U.S. This may be due in part to the fact that the higher viscosity of the liquid medium prevents the rapid reagglomeration of the solid particles after they have been deflocculated by shear and the apparent over-all viscosity falls more rapidly than expected. The decrease in thixotropy with increased temperature is rapid and the behavior is normal at all lower viscosities of the oil.

The addition of a small percentage of water to the silica systems raises the level of thixotropy and possibly increases the temperature coefficient slightly. The results were virtually identical whether 0.2 or 2.0% of water based on the system was used. No significant difference in the final pastes was noted when oils of widely differing viscosity index but of similar viscosity were used. Laboratory-prepared samples of pure silica aerogel produced grease like dispersions that were somewhat more thixotropic than their commercial analogues. This may be due to a variety of reasons such as the pH at which the silica is precipitated, concentration of the original gel, or the residual salt content. The effect of temperature on the systems was very similar however.

When the surface of the silica is made hydrocarbon in nature by a coating treatment, the system behaves in a similar manner to carbon black - oil dispersions; that is, the silica tends to become irreversibly deflocculated and a higher volume concentration is required to produce a given rigidity. Apparently, too, the interparticle bonding forces decrease rapidly with increased temperature as indicated by a rapid fall in the coefficient of thixotropy. Silica coated with alkyd resin on the other hand appears to maintain a high level of thixotropy for a given concentration but also shows a fairly high temperature coefficient. Since the coatings in these cases are probably of the order of only one molecule deep and the degree of thixotropy is virtually unaffected by shearing at room temperature, the reason for the temperature sensitivity is not obvious, unless a higher temperature dependence of surface tension at the solid-liquid interface has been effected. The effect is much more pronounced with Bentone where a deeper, more compacted hydrocarbon surface may exist. The extreme case of a sodium stearate grease is shown in Fig. 4 for comparison. The improved performance of the nonsoap dispersions is obvious, however, and indicates a possible direction for future lubricating practice.

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AN APPROXIMATE METHOD OF OBTAINING THE TRANSIENT RESPONSE FROM THE FREQUENCY RESPONSE¹

BY JAMES R. WAIT²

ABSTRACT

A novel approximate method is described for the calculation of the transient response of a system from the steady-state frequency response data. This method is particularly well suited to situations where the real part of the frequency function, when plotted on a log-frequency base, is approximated by a series of straight line segments.

In the study of amplifiers, acoustic devices, and other physical systems it is often desirable to have available some means for calculating the transient response from the steady-state frequency response. For many cases if the frequency response of a linear system is known in analytical form the corresponding form of the transient response may be obtained directly from tables of the Laplace Transforms (4) or Fourier Integrals (3). Often however the frequency response data are not given conveniently as an explicit function of frequency, in which case it is desirable to resort to a numerical or graphical procedure to obtain the transient response. Several approximate procedures (1, 2) have been developed but these are not suitable when the frequency response data are of the type that is characterized by a near linear dependence with the logarithm of the frequency.*

The steady-state transfer function $Z(i\omega)$ is the complex ratio between the response of the system to the source which varies harmonically with an angular frequency ω . The response of the same system to a unit step-function source applied at $t = 0$ is given by $A(t)$ and is related to the steady-state response by the well-known inverse Laplace integral (4) as follows:

$$[1] \quad A(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{Z(i\omega)}{i\omega} e^{i\omega t} d(i\omega)$$

where it is assumed that

$$\lim_{i\omega \rightarrow \infty} Z(i\omega)/i\omega = 0,$$

and there are no poles of $Z(i\omega)/i\omega$ in the right-hand part of the complex plane of $i\omega$ or on the imaginary axis of $i\omega$.

The complex function $Z(i\omega)$ is now written in terms of a real and imaginary part as follows:

$$[2] \quad Z(i\omega)/i\omega = R(\omega) + iI(\omega).$$

¹ Manuscript received November 14, 1952.

Contribution from the Department of Electrical Engineering, University of Toronto, Toronto, Ont.

² Now with Defence Research Board, Ottawa, Ont.

*The method of Floyd in Reference 2 is preferable to the method proposed here when there is near linear dependence with frequency rather than the logarithm of the frequency.

Now since $A(t)$ is real and equal to zero for times less than zero, it can be readily shown that

$$[3] \quad A(t) = \frac{2}{\pi} \int_0^{\infty} R(\omega) \cos \omega t \, d\omega.$$

Therefore a knowledge of $R(\omega)$ for all frequencies is sufficient to specify the transient response $A(t)$.

In many practical instances $R(\omega)$, when plotted on a base proportional to the logarithm of ω , can be approximated very well by a series of straight line segments. That is, between frequencies ω_{n-1} and ω_n ,

$$[4] \quad R(\omega) \approx A_n + B_n \log \omega,$$

so that the transient response is approximated by

$$[5] \quad A(t) = \frac{2}{\pi} \sum_1^N \int_{\omega_{n-1}}^{\omega_n} [A_n + B_n \log \omega] \cos \omega t \, d\omega$$

where the frequency range of ω from 0 to ∞ is broken into N intervals. These integrals can be expressed in terms of the sine integral

$$[6] \quad \text{Si}(z) = \int_0^z \sin z/z \, dz$$

which is tabulated by Jahnke and Emde (5). Following an integration by parts the response $A(t)$ is given by

$$[7] \quad A(t) = \frac{2}{\pi} \sum_1^N B_n [\text{Si}(\omega_n t) - \text{Si}(\omega_{n-1} t)]/t$$

where $\omega_0 = 0$. In applying this formula it is found to be convenient to take the interval ω_0 to ω_1 such that ω_1 is the angular frequency where $R(\omega)$ departs from its low frequency static value so as to make $B_1 \approx 0$. On the other hand ω_N is taken at a sufficiently large value of ω so as to have $R(\omega_N) \approx 0$. The number of intervals is chosen so as to obtain the degree of accuracy required.

To illustrate the simplicity and utility of this method an example is chosen. A frequency function is selected whose corresponding time function is known so as to provide a convenient check. In this case let

$$[8] \quad Z(i\omega) = i\omega(\alpha + i\omega)^{-1} + i\omega(2\alpha + i\omega)^{-1},$$

then

$$[9] \quad R(\omega) = \alpha(\alpha^2 + \omega^2)^{-1} + 2\alpha(4\alpha^2 + \omega^2)^{-1}.$$

The function is now normalized by putting

$$\Omega = \omega/\alpha,$$

so that

$$[10] \quad A(t) = \frac{2}{\pi} \int_0^{\infty} R(\Omega\alpha) \cos \Omega x \, d\Omega$$

where

$$[11] \quad R(\Omega\alpha) = (\Omega^2 + 1)^{-1} + 2(\Omega^2 + 4)^{-1}$$

and

$$x = \alpha t.$$

The frequency function $R(\Omega\alpha)$ is plotted in Fig. 1 against the frequency parameter Ω . The values of Ω for the limits of the approximating logarithmic curves as shown in Fig. 1 are given by

$$\begin{aligned}\Omega_1 &= 0.100, & \Omega_3 &= 1.00, & \Omega_5 &= 10.0, \\ \Omega_2 &= 0.316, & \Omega_4 &= 3.16, & \Omega_6 &= 31.6.\end{aligned}$$

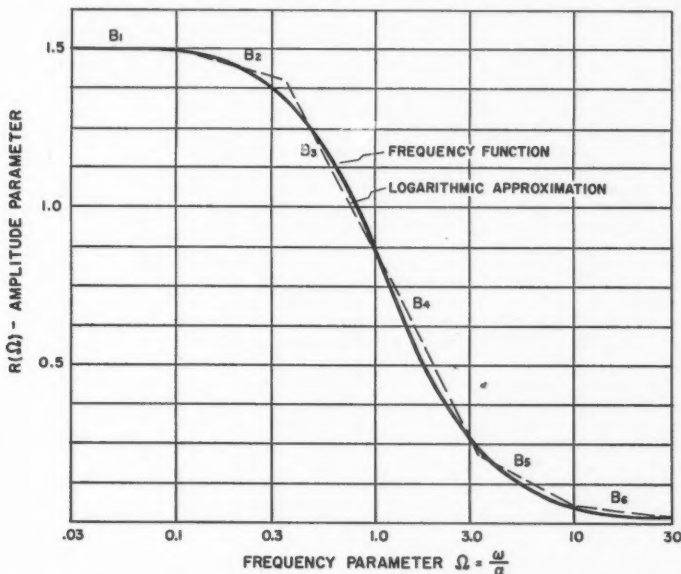


FIG. 1. The real part of a typical frequency response function and its logarithmic approximation.

The values of the slopes B_n are then easily calculated so that the transient response is approximately given by

$$\begin{aligned}\frac{\pi}{2} A(t) \approx & 0.087[\text{Si}(\Omega_2 x) - \text{Si}(\Omega_1 x)] \\ & + 0.416[\text{Si}(\Omega_3 x) - \text{Si}(\Omega_2 x)] \\ & + 0.608[\text{Si}(\Omega_4 x) - \text{Si}(\Omega_3 x)] \\ & + 0.148[\text{Si}(\Omega_5 x) - \text{Si}(\Omega_4 x)] \\ & + 0.043[\text{Si}(\Omega_6 x) - \text{Si}(\Omega_5 x)]\end{aligned}\quad [12]$$

where $x = \alpha t$.

The function $A(t)$ is plotted in Fig. 2 against the time parameter x . For this particular example the transient response can be obtained directly from the inverse Laplace integral and is given by

$$A(t) = \exp(-\alpha t) + \exp(-2\alpha t), \quad [13]$$

making use of Campbell and Foster (3) pair No. 438. This function is plotted in Fig. 2 along with the calculated results from the approximate method. The agreement between the two sets of results is quite good.

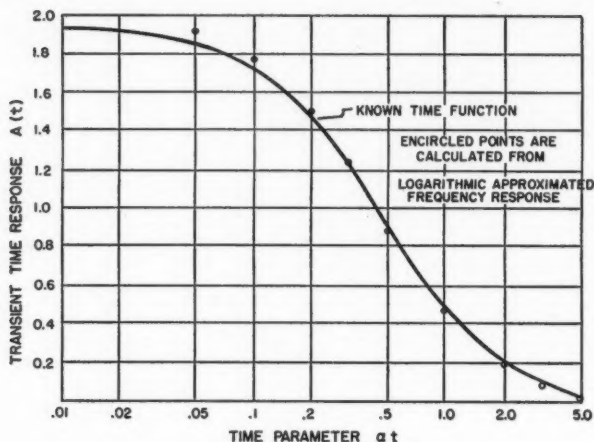


FIG. 2. The corresponding transient response functions for a unit step-function source, showing the exact curve and the calculated data.

This method can be readily extended to frequency functions $Z'(i\omega)/i\omega$ that have a simple pole of $i\omega$ and also are of the type that approach a finite value at large values of ω . For example

$$[14] \quad Z'(i\omega)/i\omega = A_0/i\omega + Z_0 + Z(i\omega)/i\omega$$

where A_0 and Z_0 are constants and $Z(i\omega)/i\omega$ satisfies the restrictions imposed on equation [1]. The transient response is then given by:

$$[15] \quad A'(t) = A_0 u(t) + Z_0 \delta(t) + A(t)$$

where

$$u(t) = 1 \text{ for } t > 0, \\ = 0 \text{ for } t < 0,$$

and $\delta(t)$ is the unit impulse function and is zero for all values of time except $t = 0$. The third term on the right side $A(t)$ is the part of the transient response that corresponds to the well-behaved part of the frequency function $Z(i\omega)/i\omega$ and is calculated by the approximate numerical method outlined above.

It might be added that the transient response $H(t)$ for a source of the form $G(t)$ applied at $t = 0$ can be calculated directly from the unit step-function response $A(t)$ by employing the superposition theorem given by

$$H(t) = \frac{d}{dt} \int_0^t G(t - \tau) A(\tau) d\tau.$$

This integration can usually be carried out conveniently by numerical means, for any specified value of time.

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THE RECEIVING LOOP WITH A HOLLOW PROLATE SPHEROIDAL CORE¹

BY JAMES R. WAIT

ABSTRACT

The relative gain of a low frequency loop with a hollow prolate spheroidal core is calculated. The case where the loop axis is coaxial with the spheroid axis of symmetry is considered. The core losses are assumed to be negligible. It is shown that a hollow core is more efficient than a solid core for the same mass of ferromagnetic material.

INTRODUCTION

In a recent paper (1) the problem of a receiving wire loop, with a core in the form of a solid spheroid of suitable magnetic material, was considered. The cases of the core axis both parallel and perpendicular to the loop axis were investigated in detail.

In this paper the effect of a hollow prolate spheroidal core is investigated. Curves are plotted showing the ratio of the induced voltage v in the circular loop with the core present to the induced voltage v_0 when the core is removed. The ratio v/v_0 is hereafter called the relative gain. As in the previous paper all losses in the core are assumed to be negligible.

GEOMETRY OF THE PROBLEM

The form of the core is shown in Fig. 1 where the inner and outer surfaces of the hollow core are confocal prolate spheroids. The core has a magnetic permeability μ_1 and the hollow space has a permeability μ which can be taken equal to that of free space. The loop of radius a is wound around the central region of the prolate spheroid as shown in Fig. 1.

CIRCULAR LOOP
with
HOLLOW PROLATE SPHEROIDAL CORE

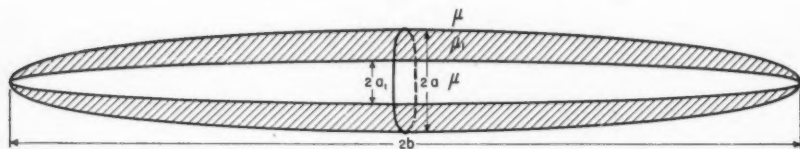


FIG. 1. The circular wire loop with a permeable core in the form of a hollow prolate spheroid.

A conventional polar coordinate system (ρ, ϕ, z) is chosen with the origin at the center of the spheroid and the z axis coincident with the longitudinal

¹ Manuscript received February 12, 1953.

Contribution from the Radio Physics Laboratory, Defence Research Board, Ottawa, Ontario.

axis of the spheroid. It is now convenient to introduce prolate-spheroidal coordinates whose family of spheroids are

$$[1] \quad \frac{\rho^2}{c^2(\eta^2 - 1)} + \frac{z^2}{c^2\eta^2} = 1$$

and whose family of hyperboloids are

$$[2] \quad \frac{\rho^2}{c^2(1 - \delta^2)} + \frac{z^2}{c^2\delta^2} = 1$$

where c is constant. The family of spheroids is chosen to be confocal with the surfaces of the core. If b is the semimajor axis and a is the semiminor axis, then the outer surface of the core is specified by

$$[3] \quad \eta = \eta_0 = b(b^2 - a^2)^{-\frac{1}{2}}$$

and the inner surface of the core is specified by

$$[4] \quad \eta = \eta_1 = \left[1 + (\eta_0^2 - 1) \frac{a_1^2}{a^2} \right]^{\frac{1}{2}}$$

where a_1 is the semiminor axis of the inner surface. The semimajor axis b_1 of the inner surface is then given by

$$[5] \quad b_1 = b\eta_1/\eta_0.$$

The thickness of the ends of the core is then given by

$$b - b_1 = b\{1 - [1 - (a/b)^2(1 - a_1^2/a^2)]^{\frac{1}{2}}\}$$

and if $b/a > 5[1 - (a_1^2/a^2)]^{\frac{1}{2}}$ the following expression is accurate to within an error of 1%:

$$[6] \quad b - b_1 = b[1 - (a_1^2/a^2)]/2(b/a)^2.$$

The volume V_c of the core material is given by

$$[7] \quad V_c = \frac{4}{3} \pi (a^2b - a_1^2b_1)$$

and for $b/a > 4$

$$[8] \quad V_c = \frac{4}{3} \pi a^2b \left(1 - \frac{a_1^2}{a^2} \right)$$

so that the volume and therefore the weight of the hollow core is reduced by the ratio $(1 - a_1^2/a^2)$ relative to the solid core of the same outer dimensions.

SOLUTION

The method of obtaining an expression for the voltage induced in the loop is a direct extension of the analysis for the solid core in the previous paper (1). A uniform magnetic field, whose component is $H_0 \exp(i\omega t)$ in the direction of the longitudinal axis, is applied to the spheroid. Since all dimensions are assumed to be much less than a wave length, the fields are a solution of Laplace's equation.

For the same reasons as in the previous paper the resultant magnetic potential F outside the spheroid can be written

$$[9] \quad F = P_1(\delta) cH_0 [P_1(\eta) + BQ_1(\eta)]$$

for $\eta \geq \eta_0$. Also it was shown that the relative gain is given by

$$[10] \quad v/v_0 = 1 + BQ_1'(\eta_0)$$

where $v_0 = i\mu\omega\pi a^2 H_0 N$, and N is the number of turns of the loop. The corresponding potentials F_1 and F_2 in the core and in the hollow space respectively are of the form

$$[11] \quad F_1 = P_1(\delta)A_1[P_1(\eta) + B_1Q_1(\eta)]$$

for $\eta_1 \leq \eta \leq \eta_0$

$$[12] \quad \text{and} \quad F_2 = P_1(\delta)A_2P_1(\eta)$$

for $\eta_1 \geq \eta \geq 1$.

The boundary conditions are that the magnetic potential and normal flux are continuous; these are written

$$[13] \quad \left. \begin{aligned} F &= F_1 \\ \mu \frac{\partial F}{\partial \eta} &= \mu_1 \frac{\partial F_1}{\partial \eta} \end{aligned} \right\} \text{at } \eta = \eta_0,$$

$$[14] \quad \left. \begin{aligned} F_1 &= F_2 \\ \mu_1 \frac{\partial F_1}{\partial \eta} &= \mu \frac{\partial F_2}{\partial \eta} \end{aligned} \right\} \text{at } \eta = \eta_1.$$

The unknown coefficients can now be solved to obtain

$$[15] \quad B_1 = - \frac{(\mu_1 - \mu)\eta_1}{\eta_1\mu_1 Q_1'(\eta_1) - \mu Q_1(\eta_1)}$$

and

$$[16] \quad B = - \frac{\eta_0(\mu_1 - \mu) + B_1[\mu_1\eta_0 Q_1'(\eta_0) - \mu Q_1(\eta_0)]}{[\mu_1 Q_1(\eta_0) - \mu\eta_0 Q_1'(\eta_0)] + B_1[(\mu_1 - \mu)Q_1(\eta_0)Q_1'(\eta_0)]}$$

where the identities

$$[17] \quad P_1(\eta) = \eta \text{ and } P_1'(\eta) = 1$$

are used.

The relative gain given by equation [10] is now computable, using the expression derived for B in equation [16]. The following two identities are found to be useful if tables are not available for the Legendre functions:

$$[18] \quad Q_1(\eta) = \eta \coth^{-1}\eta - 1,$$

$$[19] \quad Q_1'(\eta) = \coth^{-1}\eta + \eta(1 - \eta^2)^{-1}.$$

Curves are now plotted for the relative gain v/v_0 for b/a ranging from 2.0 to 100, and are shown in Figs. 2 to 5. Various values of the ratio a_1/a are specified. The case where $a_1/a = 0$ corresponds to the solid core. The four sets of curves correspond to four typical permeability values, of commercially available ferromagnetic materials (i.e. $\mu_1/\mu = 20, 50, 200$, and 500).

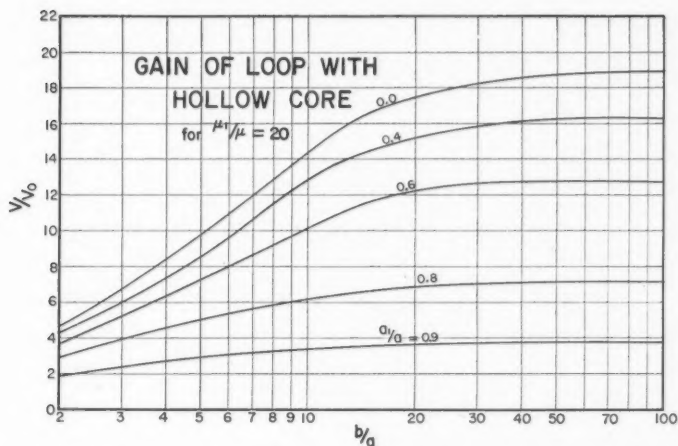


FIG. 2. The relative gain of the loop for a relative permeability of the core material of 20.

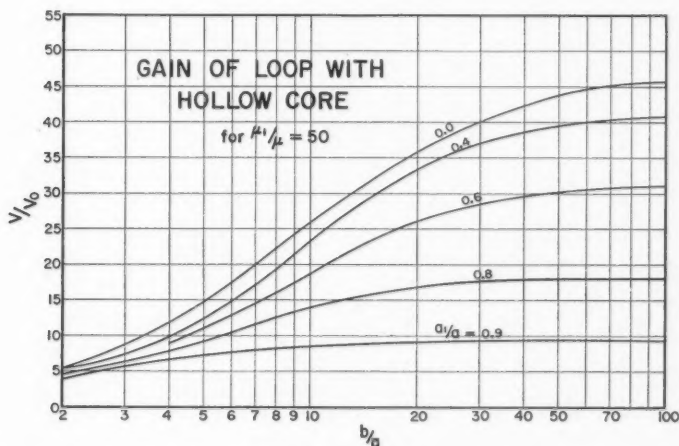


FIG. 3. The relative gain of the loop for a relative permeability of the core material of 50.

As the core becomes relatively long corresponding to large values of b/a , the gain approaches asymptotically the value

$$[20] \quad \left(\frac{V}{V_0} \right)_{b/a \rightarrow \infty} = \frac{\mu_1}{\mu} \left(1 - \frac{a_1^2}{a^2} \right)$$

which could be derived directly by considering the core to be equivalent to a thick cylindrical shell of infinite length whose inner and outer radii are a_1 and a respectively.

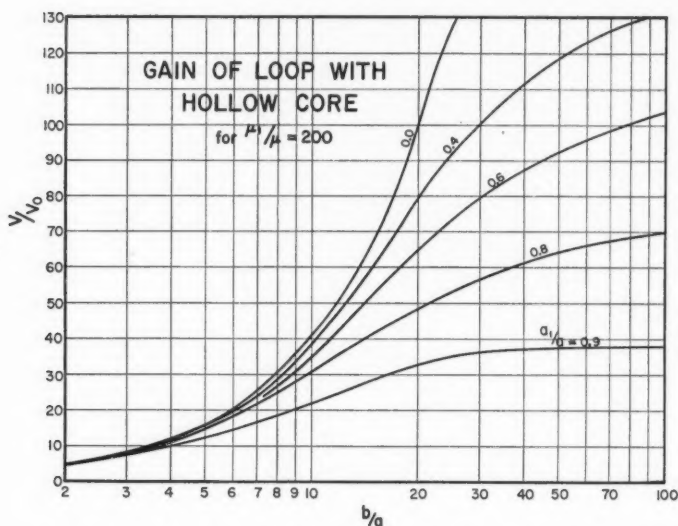


FIG. 4. The relative gain of the loop for a relative permeability of the core material of 200.

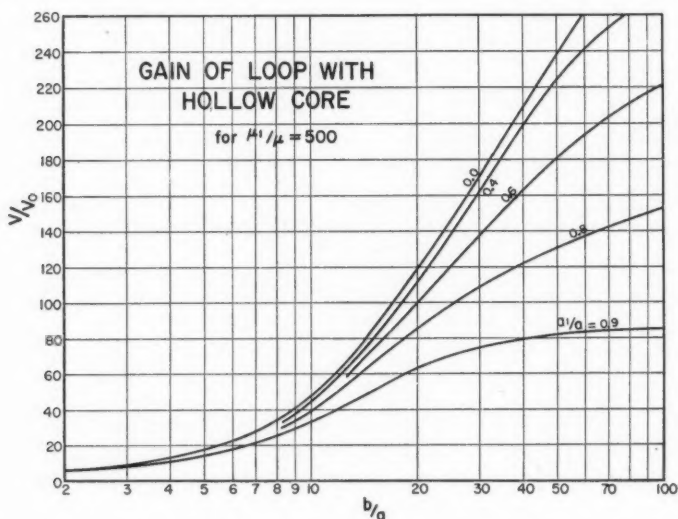


FIG. 5. The relative gain of the loop for a relative permeability of the core material of 500.

CONCLUSIONS

From the spheroidal model that has been chosen, it is apparent that a hollow core of finite length would be more efficient than a solid core of the same mass of magnetic material. From equations [8] and [20], it is clear that there is no

improvement over a solid core of the same weight in the limiting case of a very long spheroid. The graphs show however, that there is some improvement for cores of practical length, particularly for high permeability core materials. The graphs also show that the advantage of a hollow core increases with decreasing values of b/a .

ACKNOWLEDGMENT

The assistance received from Mr. M. C. Keating in preparing the graphs is greatly appreciated.

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THE THIOBARBITURIC ACID TEST FOR BUTTERFAT OXIDATION¹

BY D. A. BIGGS AND L. R. BRYANT²

ABSTRACT

The method for oxidative deterioration in fat products proposed by Dunkley and Jennings has been investigated and modified. Time of reaction, pH of reaction mixture, presence of oxygen in the reaction chamber, and presence of an emulsifying agent in the reaction mixture are shown to influence the amount of color produced. The modified method can be applied to the determination of oxidation in powdered whole milk, Cheddar cheese, and butter. Interferences from colored materials in the sample can be eliminated by running blank determinations. Correction can be made for interference caused by lactose in milk powder by reference to a predetermined correction chart. Duplicate determinations on these products indicated good reproducibility. The results on milk powders showed a correlation between test values and organoleptic flavor scores and indicated that the test is capable of measuring degrees of oxidation below the level of organoleptic sensitivity.

INTRODUCTION

Patton and Kurtz (4) have suggested that the 2-thiobarbituric acid (TBA) test could be used advantageously in testing for oxidative deterioration in a wide variety of fats and fat-containing foods. The work of Bernheim, Bernheim, and Wilbur (1) indicated that the red pigment formed in the test is a reaction product of TBA and oxidized unsaturated fatty acids or their degradation product(s). A review of the literature has revealed that these acids have not been used in efforts to determine the effect of experimental conditions on the course of the reaction. Published absorption curves may therefore include absorptions from products of TBA reaction with nonfatty materials. Time of heating does not affect color development similarly in the reactions with milk (3) and with butterfat (4). The effect of pH has been reported only for the reaction with milk.

Several points of possible importance have not been investigated previously. Although the color-forming reaction is carried out at the temperature of boiling water, no one has yet explored the possibility that the fat may be further oxidized during this heating period. The relative rates of reaction of oxidized unsaturated fatty acids known to give the test have not been ascertained. No attempt has been made to disperse the fat in the reaction mixture.

In the present investigation the effects of the various experimental factors upon the TBA reaction have been studied with oxidized oleic acid, oxidized 60% linoleic acid, and oxidized 60% methyl linoleate. An attempt has been made to arrive at and apply optimum conditions to the testing of butter, Cheddar cheese, and whole milk powder.

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Contribution from the Graduate School, University of Toronto, Toronto, Ontario. Adapted for publication from a thesis submitted to the Graduate School, University of Toronto, by D. A. Biggs, in partial fulfillment of the requirements for the degree of Master of Science in Agriculture.

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REAGENTS

TBA reagent—0.025 molar 2-thiobarbituric acid in molar phosphoric acid.

10% alkylidimethylbenzylammonium chloride solution—commercial "Roccal".

Isoamyl alcohol—Baker and Adamson reagent grade.

Pyridine—British Drug Houses, certified 99%.

Extraction mixture—2: 1 mixture of isoamyl alcohol and pyridine.

Purified nitrogen—last traces of oxygen removed by method of Brady (2).

Oleic acid; 60% linoleic acid; 60% methyl linoleate—Nutritional Biochemicals Corporation. To oxidize these materials air was passed through them for periods ranging from 24 to 72 hr. During the oxidation period they were exposed to the rays of a 60 w. tungsten lamp.

METHOD

In order to exert a more complete control over reaction conditions it was necessary to modify the procedure used by Dunkley and Jennings (3). The TBA reaction was carried out in a 300 ml. three neck distilling flask fitted with condenser, mercury seal, motor driven stirrer, and stopper. A weighed quantity of sample and a definite volume of reagent mixture were first placed in the flask and the stirrer started. If it was desired to exclude atmospheric oxygen from the reaction, purified nitrogen was passed into the flask for 15 min. prior to, as well as during, the heating period. The reaction mixture was heated with a boiling water bath. A 10 ml. aliquot was withdrawn at various intervals and transferred to a 40 ml. centrifuge tube containing an equal volume of extracting mixture. The centrifuge tube was equipped with a motor driven stirrer and cooled by means of a cold water bath. After cooling and extracting, the mixture was centrifuged. A portion of the solvent layer was then transferred to a 1 cm. cell and the optical density determined at 535 m μ by means of a Beckman model B spectrophotometer. Distilled water was used as a blank. pH measurements when required were made with a Beckman model H meter on the cooled reaction mixture after the conclusion of the tests.

EFFECT OF ADDITION OF EMULSIFYING AGENT

This effect was studied by adding 1 part of a 10% solution of alkylidimethylbenzylammonium chloride to 14 parts of TBA reagent. Comparison of the two curves for pH 1.1 in Fig. 1 shows that the emulsifying agent doubled the amount of color formed and increased the rate of reaction. Without the emulsifying agent the optical densities developed in 10 and 30 min. were 56 and 86% respectively of the optical density developed in one hour. With the emulsifying agent these optical densities were respectively 80 and 92% of the optical density developed in one hour.

The spectral absorption curve of the reaction products was the same as that shown in Fig. 2 for the isolated red compound,* indicating that no inter-

*The red compound was isolated by the following method: About $\frac{1}{2}$ gm. of oxidized oleic acid was added to a mixture of 140 ml. of TBA reagent and 10 ml. of emulsifying agent. The mixture was heated for three hours on a boiling water bath, during which time it was stirred continuously. After standing for about 16 hr. a quantity of red precipitate settled to the bottom of the flask. This precipitate, after separation from the mixture by centrifugation, was washed three times with cold water, three times with warm ethyl ether, and dried. Fig. 2 shows the spectral absorption curve for a solution of this product in isoamyl alcohol.

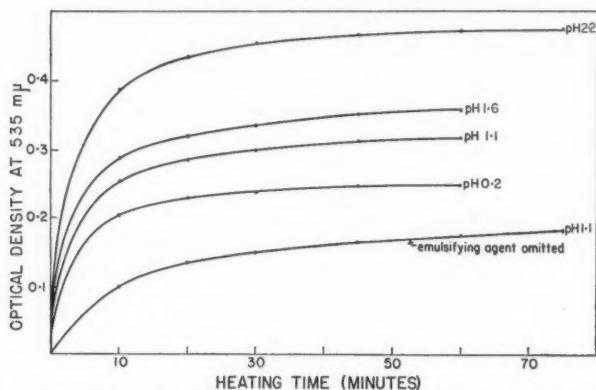


FIG. 1. A comparison of rates of color development at various pH's for the TBA reaction with 60% linoleic acid. (Reaction under nitrogen.)

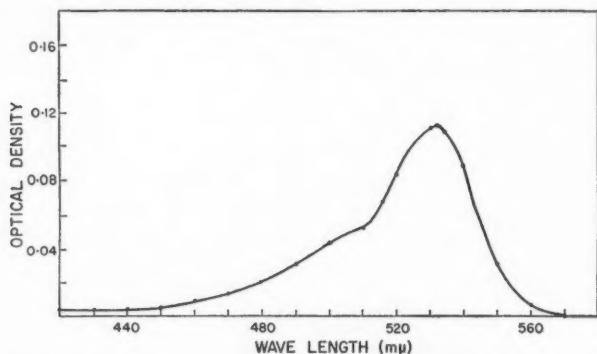


FIG. 2. Spectral absorption curve for the red compound isolated from the TBA reaction with oxidized oleic acid.

ference was introduced by the addition of this emulsifying agent. It was therefore used in all subsequent studies.

EFFECT OF OXYGEN ON THE REACTION

This factor was investigated by comparing reactions carried out in the presence of nitrogen and air. Fig. 3 shows that in the presence of nitrogen the optical density was at a maximum in one hour whereas, in the presence of air, the optical density continued to increase at an almost constant rate for an additional period. It was found that after four and one half hours of heating the hour rate of optical density increase was only slightly reduced. The error introduced by carrying out the reaction in the presence of air did not appear to bear any fixed relationship to the degree of oxidation of the samples, although in general the amount of error was greater with the more highly oxidized samples. From the above evidence it was concluded that the reaction should preferably be carried out in the absence of air.

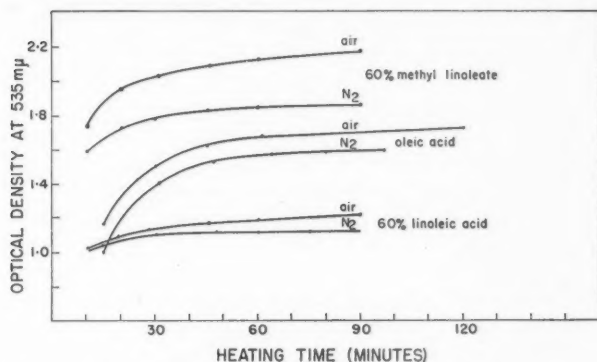


FIG. 3. A comparison of TBA reactions in the presence of air and nitrogen.

TIME REQUIRED FOR DEVELOPMENT OF MAXIMUM COLOR

Examination of Fig. 3 reveals that when the TBA reaction is carried out under nitrogen the heating times required to develop the maximum optical density with oxidized oleic acid, oxidized 60% methyl linoleate, and oxidized 60% linoleic acid were 60 min., 45 min., and 30 min., respectively. The one-hour heating period developed the maximum optical density with each of these materials and was therefore considered to be optimum for the test.

EFFECT OF pH ON COLOR DEVELOPMENT

This effect was studied by varying the phosphoric acid content of the TBA reagent. In this experiment isoamyl alcohol alone was used to extract the colored product, as it was found that the solubility of pyridine in the aqueous phase increased as the pH was decreased. The results, illustrated in Fig. 4,

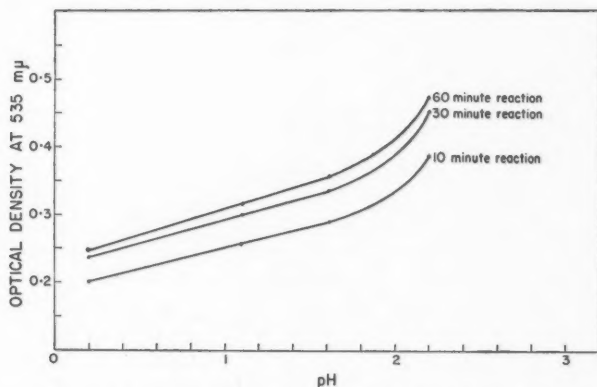


FIG. 4. The effect of pH on amount of color developed in the TBA reaction with 60% linoleic acid. (Reaction under nitrogen.)

show that the amount of color developed in one hour increased with pH in the range from 0.2 to 2.2. The relationship between heating time and color development in this pH range is indicated in Fig. 1. It is clear from the shape of these curves that the color developed in an hour is the maximum color, and that it is the amount and not the rate of maximum color development that is affected by changes in pH. Conversely, when the pH was increased to values above 2.2 it was found that longer heating periods were required to develop the maximum color. The maximum color was therefore developed in the least time at pH values between 0.2 and 2.2. From examination of Fig. 4 it is evident that the influence of changes in pH on the amount of color formed is at a minimum in the pH range from 0.2 to 1.6. Sensitivity considerations therefore indicated that a pH of 1.6 or slightly lower would be most suitable for the test.

INTERFERENCES

In order to reveal interferences from the nonfatty portion of milk, cheese, and butter, the absorption curve of the reaction products of TBA and each material was compared with the absorption curve of the isolated red pigment shown in Fig. 2. The spectral curve of the reaction products was arrived at by subtracting the absorptions of the reagent blank extract and the sample blank* extract from the absorption of the sample extract. The absorption curve of the butter reaction products showed no evidence of interference. That of the cheese reaction products indicated some interference. The amount of this interference was approximated by reducing the absorption curve of the red compound in size so that it would just fit under the absorption curve of the cheese reaction products.** At the 535 m μ wave length the gap between the two curves represented 0.01 optical density unit. The concentration of cheese used was 3 gm. in 75 ml. of reagent mixture and it was therefore assumed that this concentration would lead to interference of the above order. The previously mentioned optimum conditions were adopted for the testing of butter and cheese.

The absorption curve of the whole milk powder reaction products entirely masked the characteristic curve of the red compound. When lactose was submitted to the test its reaction products produced absorption curves almost identical to those obtained with the milk powder. It therefore became evident that lactose was responsible for the interference. It was found that the amount of this interference increased with the length of the heating period, with decreasing pH, and with an increased supply of oxygen in the reaction vessel. Reducing the heating period from one hour to 10 min. and the phosphoric acid strength of the reagent from one to one-third molar gave a linear relation between the lactose concentration and the amount of interference. When various amounts of lactose were added to milk powder the same linear relation was shown to exist between the increase in lactose concentration and the increase in interference. A knowledge of the approximate amount of lactose in a sample therefore permitted calculation of the amount of interference from a predetermined

*Thiobarbituric acid omitted from reagent mixture.

**It has been reported previously (3) that measurements of the absorption of the red compound conform with Beer's law.

correction chart. Milk powders tested were therefore heated 10 min. with the reagent containing this smaller amount of acid. The heating period is critical in the 10 min. test and should be accurately timed. Under the conditions described and in the absence of air the amount of interference was 0.0075 optical density unit for a lactose concentration of 1 gm. in 25 ml. of reagent mixture. With the Dunkley and Jennings procedure (3) the same concentration gave a lactose interference of 0.016 optical density unit.

TBA VALUE AND SAMPLE CONCENTRATION

The relationship between sample concentration and the TBA value obtained was investigated for all three materials. With 75 ml. of reagent mixture straight line relationships were obtained for concentrations up to 2, 5, and 6 gm. of butter, whole milk powder, and cheese respectively.

RESULTS AND DISCUSSION

Duplicate determinations made on a number of samples of these three products at various stages of oxidation are shown in Tables I, II, and III. The data in

TABLE I
REPRESENTATIVE RESULTS FOR THE TBA TEST ON BUTTER

Days after adding 10 p.p.m. of copper	Optical density at 535 m μ *	
	1	2
0	0.034	
3	0.040	
4	0.041	
5	0.048	0.047
7	0.054	0.054
8	0.056	0.056

*Optical densities of reagent and sample blanks have been subtracted. Values shown are for sample concentrations of 1 gm. in 75 ml. reagent mixture.

TABLE II
REPRESENTATIVE RESULTS ILLUSTRATING THE REPRODUCIBILITY OF TBA DETERMINATIONS ON MILK POWDERS

Description of sample	Optical density at 535 m μ *	
	1	2
Fresh	0.007	0.007
Slightly oxidized	0.014	0.013
Oxidized	0.026	0.026
Very oxidized	0.079	0.084
Oxidized	0.039	0.039
Oxidized	0.039	0.039
Very oxidized	0.082	0.085

*Optical densities are for 3-gm. samples in 75 ml. of reagent mixture. The following optical densities were subtracted—(a) 0.003 for reagent blank. (b) 0.002 for sample blank. (c) 0.003 for lactose correction.

TABLE III

REPRESENTATIVE RESULTS ILLUSTRATING THE REPRODUCIBILITY OF TBA DETERMINATIONS ON CHEDDAR CHEESE

Age of sample in months	Lot number	Reaction under:	Optical density at 535 m μ *	
			1	2
1	151	N ₂	0.015	0.014
3	127	N ₂	0.012	0.011
4	110	N ₂	0.014	0.014
8	195	N ₂	0.014	0.016
15	183	N ₂	0.018	0.018
18	141	N ₂	0.049	0.048
1	151	Air	0.026	0.025
3	127	Air	0.021	0.020
4	110	Air	0.024	0.025

*Optical densities are for 3-gm. samples in 75 ml. of reagent mixture. Optical densities of sample and reagent blanks have been subtracted.

each case indicated satisfactory reproducibility. The values for the Cheddar cheese samples were only slightly higher than the approximate interference error and indicated that the butterfat in these cheeses was not appreciably oxidized during the first year of storage. The daily changes in an artificially oxidized sample of butter were measurable. The samples of milk powder tested gave TBA values which correlated with the determination of organoleptic flavor made by the Borden Company Limited. The value for the slightly oxidized milk powder sample is sufficiently high that the method can distinguish degrees of oxidation below the level of organoleptic sensitivity.

SUMMARY

The presence of the emulsifying agent alkyldimethylbenzylammonium chloride in the TBA reagent increases the rate and amount of color formation. Optical density reaches a maximum in an hour in a nitrogen atmosphere at pH values between 0.2 and 2.2. A pH of 1.6 is favorable from considerations of sensitivity and precision.

Heating periods of less than an hour will favor determination of oxidation in fatty acids less saturated than oleic. The presence of air in the reaction vessel appears to cause further oxidation of fat during the heating period, and also increases the amount of interference encountered in testing samples containing lactose. In testing Cheddar cheese, butter, and milk powder this interference is the only interference of any consequence which cannot be eliminated by the running of blank determinations. In the presence of lactose the heating period must be limited to 10 min. in which case correction can be made for lactose interference if the approximate lactose content of the sample is known.

The method described is of particular value for testing dairy products since determinations can be made directly on the sample without separation of the

fat. It is probable that the test could easily be adapted to the measurement of oxidative deterioration in nonsugar containing fatty materials such as lard and shortening.

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THE HEAVY METAL CONTENT OF GELLING AND STABILIZING AGENTS¹

By J. C. BARTLET, ETHEL LIST, MARGARET PAGE, AND R. A. CHAPMAN

ABSTRACT

The arsenic, lead, zinc, and copper content of samples of agar, gelatin, Irish moss gelose, vegetable gums, and other stabilizing agents used in the food industry has been determined. Some samples of agar were found to contain appreciable quantities of zinc, which was not uniformly distributed, and therefore the sampling of shredded agar was studied. To obtain representative samples, a sampling tool was designed. Agar was found to contain as much as 450 parts per million of zinc and 16 p.p.m. of lead. Amounts up to 125 p.p.m. of zinc and 6 p.p.m. of lead were found in gelatin. Irish moss gelose (carrageen) contained less than 100 p.p.m. of zinc, up to 15 p.p.m. of lead, and 30 p.p.m. of copper. The amounts of lead, copper, zinc, and arsenic found in samples of sodium pectate, sodium alginate, liquid pectin, gum karaya, gum arabic (gum acacia), locust bean gum (carob gum), sodium carboxymethylcellulose, and methylcellulose are also given. With the exception of one sample of locust bean gum, no sample tested contained more than 2.0 p.p.m. of arsenic. One stabilizing mixture and one sample of sodium alginate contained excessive amounts of lead.

INTRODUCTION

Large quantities of gelling and stabilizing agents are at present being used in the manufacture of food products in Canada. Gelatin, a widely used gelling agent, is produced from bones and hides, and during the production may become contaminated with heavy metals. During the early part of the twentieth century, gelatin was reported to contain as much as 30 parts per million of arsenic, 260 p.p.m. of copper, and 1341 p.p.m. of zinc (3). Since that time the methods of manufacturing gelatin have improved to such an extent that such heavy contamination is no longer encountered; however, very few data for the metal content of gelatin have been published since 1923.

Agar, Irish moss (carrageen), and the alginates are produced from extracts of seaweeds and, during the extraction and subsequent processing, opportunities arise for contamination by heavy metals. The vegetable gums such as gum arabic and gum karaya are produced by relatively primitive means but with a minimum of processing which could introduce metallic contamination. The only recent values for heavy metals in these materials are reported by Morgan (5) and have been summarized in Table I. LaWall and Harrisson (4) found 1.8 to 9 p.p.m. of arsenic in 12 samples of Irish moss. Pectin prepared from fruits is used to a large extent in the jam industry and since copper, lead, and arsenic compounds are used in insecticides and fungicides, some contamination from spray residues might be expected. Sodium carboxymethylcellulose and methylcellulose are also used as stabilizing agents but in this case the heavy metal content would depend on metallic contamination during processing. However, a review of the literature revealed no published values for the heavy metal content of these products.

¹ Manuscript received February 25, 1953.

Contribution from Food and Drug Laboratories, Department of National Health and Welfare, Ottawa, Canada.

TABLE I
HEAVY METAL CONTENT OF GUMS AND STABILIZING AGENTS (5)

Material	Pb, p.p.m.	Cu, p.p.m.	Zn, p.p.m.
Agar	2.9	Nil	9.7
Gum arabic	1.8	4.0	3.0
Carob gum	2.0	8.0	1.0
Gum ghatti	2.8	1.3	4.2
Irish moss	57	36	65
Sodium alginate	7.8	10	25
Tragacanth	4.9	23	55
Commercial vegetable gelatin ¹	6.7	20	203

¹The composition of "commercial vegetable gelatin" was not given.

In view of the lack of published information in this field, a survey has been conducted to determine the heavy metal content of stabilizing agents used in Canadian food products.

ANALYTICAL METHODS

Arsenic

Arsenic was determined by a Gutzeit procedure (1) after acid digestion of the gelling agent or after separation as magnesium ammonium arsenate with phosphate as a carrier (2). The latter method gave satisfactory recovery of known amounts of arsenic added to agar and Irish moss, and was used for these two materials and gelatin.

Lead, Copper, and Zinc

Samples were digested with nitric, sulphuric, and perchloric acids. To the sample solution, 2.0 mgm. of bismuth was added and the heavy metals precipitated as sulphides with the bismuth acting as a carrier. The sulphides were mixed with graphite powder and the metals determined spectrographically employing a d-c. arc at 6 amp. The densities of lines of bismuth, lead, copper, and zinc were measured with a microphotometer, intensity ratios of impurity lines to a bismuth line were calculated, and the amount of each element was determined from standard curves.

SAMPLING

Except for agar and liquid pectin, all the samples examined were in the form of a powder and were sufficiently homogeneous that no special sampling precautions were necessary. However, a large portion of the agar was shredded, and preliminary work showed that these samples were far from homogeneous. Because of this variation, an investigation was made to develop a satisfactory sampling procedure for this product.

Laboratory Sampling

Analysis of 1 gm. portions from samples of shredded agar as received in the laboratory gave widely different results for zinc. Values obtained on 10

representative samples are given in Table II. In some cases there is more than a 10-fold variation in the zinc content of portions of the same sample. Powdered agar is more homogeneous with little variation between 1 gm. samples.

In view of this variability, the following laboratory sampling procedure was adopted for shredded agar. The whole of the agar sample as received was chopped and mixed in a dry state in a Waring Blendor. Ten grams of the chopped agar was dissolved in 10% nitric, and a 1 gm. aliquot taken for analysis. Duplicate 10 gm. samples gave satisfactory agreement by this procedure as indicated in Table II.

TABLE II
ZINC CONTENT OF REPLICATE SAMPLES OF AGAR

Type of agar	Zn, p.p.m.		
	1	2	3
1 gm. samples			
Powder	85	100	100
"	80	80	90
Shred	15	35	230
"	15	65	200
"	20	20	45
"	70	150	200
"	20	280	500
"	120	130	280
"	15	60	80
"	15	140	170
10 gm. samples			
Flake	60	70	
Powder	85	80	
"	250	250	
Shred	250	230	
"	80	100	
"	125	130	
"	140	140	
"	25	25	

Sampling of Agar Bales

Since the zinc content of agar within the small laboratory samples varied widely, a thorough investigation into the sampling procedure was considered desirable.

Agar is usually shipped in bales weighing about 100 lb. and measuring approximately 28 in. \times 28 in. \times 12 in. The bales examined consisted of a number of layers compressed together so tightly that the layer boundaries were ill-defined. To sample such bales, a special bit was designed which consisted of a piece of stainless steel tubing 13.5 in. long, O.D. 0.92 in., I.D. 0.81 in. with one end sharpened to a serrated cutting edge. The other end was threaded to fit an adapter so that it could be used with an ordinary carpenter's brace. Using this bit, samples could be taken as a core through the entire thickness of the bale.

With the aid of this tool, two bales of agar were examined in detail. Bale No. 1 was of a uniform light straw color except for one corner which was discolored through water damage. Thirteen "grab" samples and seven "core" samples were taken from this bale. These samples contained approximately 2 p.p.m. of lead and less than 15 p.p.m. of zinc, except for the sample from the discolored corner which contained 10 p.p.m. of lead and 150 p.p.m. of zinc.

Bale No. 2 had ill-defined layers of darker agar throughout. Fifteen grab samples weighing from 2.8 to 13.2 gm. and five core samples of approximately 35 gm. were obtained. The amounts of zinc and lead found are given in Table III. The core samples appear to be relatively uniform but the "grab" samples

TABLE III
ZINC AND LEAD CONTENT OF AGAR SAMPLES FROM BALE NO. 2

Type of sample	Zn, p.p.m.	Pb, p.p.m.
Core	505	15
"	440	12
"	475	16
"	490	14
"	475	12
Grab	190	5
"	100	4
"	420	11
"	420	17
"	850	33
"	240	10
"	730	22
"	750	24
"	510	16
"	250	12
"	235	6
"	235	13
"	350	10
"	560	20
"	460	15

vary over a wide range. There is a rough correlation between the zinc and the lead values for these samples indicating that the zinc and lead contamination may have come from the same source.

To determine the variation between bales in a shipment, 10 bales of one shipment were sampled, three core samples being taken from each bale. The average zinc content of three determinations on each sample and the average lead values are given in Table IV. All figures including results for replicate determinations on each sample were analyzed statistically; the results are shown in Table V. Unlike the core samples from Bale No. 2 samples of the same bale showed a significant variation in zinc and lead content as did also samples from different bales within the shipment.

Because of the variation shown in Tables II to IV, sampling of a shipment of agar will necessitate a compromise between desired precision and a reason-

TABLE IV

AVERAGE ZINC AND LEAD CONTENT (P.P.M.) OF CORE SAMPLES FROM A SHIPMENT OF 10 BALES

Bale No.	Sample No.					
	1		2		3	
	Zn	Pb	Zn	Pb	Zn	Pb
1	205	5.3	105	4.7	305	4.9
2	250	5.3	215	5.0	215	4.6
3	165	2.9	215	4.0	215	4.1
4	255	3.5	185	2.8	180	4.3
5	225	7.1	270	6.7	125	4.4
6	205	3.7	275	5.3	170	4.7
7	205	4.4	220	4.6	225	5.4
8	285	5.0	260	3.9	285	5.1
9	280	4.7	315	5.8	250	5.0
10	280	10.5	310	10.0	335	8.8

TABLE V

ANALYSIS OF VARIANCE FOR ZINC AND LEAD DETERMINATION

Element	Source of variation	Degrees of freedom	Mean square	Theoretical mean square
Zn	Between bales	9	13,936.49	$\sigma^2 + 3\sigma_W^2 + 9\sigma_B^2$
	Within bales	20	7,131.74	$\sigma^2 + 3\sigma_W^2$
	Replicates	59	180.72	σ^2
Pb	Between bales	9	27.6617	$\sigma^2 + 3\sigma_W^2 + 9\sigma_B^2$
	Within bales	20	1.7458	$\sigma^2 + 3\sigma_W^2$
	Replicates	55	0.3016	σ^2
Zinc $\sigma^2 = 180.72$			Lead $\sigma^2 = 0.3016$	
$\sigma_W^2 = 2317.01$			$\sigma_W^2 = 0.4814$	
$\sigma_B^2 = 756.08$			$\sigma_B^2 = 2.8795$	

able number of samples. Since few shipments of agar to Canada consist of more than 10 bales, it should be possible to sample each bale. If N_1 represents the number of bales in the shipments and N_2 samples are drawn from each, with a single determination on each sample, then the variance of the average value of zinc will be:

$$\text{var. } \bar{X} = \frac{\sigma_e^2 + \sigma^2}{N_1 N_2} = \frac{2497.73}{N_1 N_2}$$

and the standard error of the average value of zinc will be:

$$\text{S.E.} = \sqrt{\frac{2497.73}{N_1 N_2}}$$

Table VI gives the expected standard error for various values of N_1 and N_2 . These data indicate that, if the desired precision is approximately $\pm 20\%$ or less, five core samples should be drawn from a shipment of one bale, three from each bale for a shipment of two bales and two from each bale for a

TABLE VI
 PRECISION OF MEAN ZINC VALUES IN AGAR

No. of bales	No. of samples from each	S.E. of Zn values, p.p.m. (at 234 p.p.m. level)	S.E., %
1	2	35	15
	3	29	12
	4	25	11
	5	22	10
2	2	25	11
	3	20	9
	4	18	8
3	2	20	9
	3	17	7
4	2	18	8
5	2	16	7
6	2	14	6
7	2	13	6
8	2	13	6
9	2	12	5
10	2	11	5

shipment of more than two bales. For example, in a shipment consisting of two bales, if three samples are drawn from each bale, the average value for zinc will be correct to $\pm 18\%$ (twice the standard error). These calculations are based on the assumption that the segregation of zinc in the bales of a shipment will not be greater than the variation of zinc in the shipment examined. If the zinc content of a shipment varies to a greater extent, the precision will be overestimated. Since the variation of lead is less than that of zinc, such a sampling scheme will also give adequate precision for the lead values.

RESULTS

Agar

The amounts of heavy metals found in 31 samples of agar are given in Table VII. The values reported for zinc in shredded agar are representative of the laboratory samples only, and do not necessarily represent the true values for the bales from which the samples were taken. The country of origin is given where known. Except for samples No. 12 and 14, which also contained excessive zinc, not more than 8 p.p.m. of lead was found in any sample. As may be seen, agar may contain appreciable amounts of zinc with 19% of the samples having more than 200 p.p.m. and 39% more than 100 p.p.m. Sample No. 1 contained 10 p.p.m. of copper but all others contained less than this amount. Silver (50 p.p.m.) was found in sample No. 22 but no other sample contained more than 2 p.p.m.; tin was detected only in sample No. 2.

Gelatin

The arsenic, lead, and zinc content of 12 samples of gelatin is given in Table VIII. The country of origin of three samples is not known. No sample contained more than 8 p.p.m. of lead, and only one sample contained more than 100 p.p.m. of zinc. The four samples with more than 50 p.p.m. of zinc were from the same manufacturer. There was less than 10 p.p.m. of copper in every sample.

TABLE VII
HEAVY METAL CONTENT OF AGAR

Sample No.	Type	Country of origin	As, p.p.m.	Pb, p.p.m.	Zn, p.p.m.
1	Powder	New Zealand	0.5	8	120
2	"	"	<0.5	8	250
3	Flake	"	<0.5	7	45
4	Powder	U.S.A.	<0.5	3.5	70
5	Flake	"	<0.5	1.5	30
6	Flake	Mexico	<0.5	2	65
7	Shred	Japan	<0.5	3.5	60
8	"	"	<0.5	3	15
9	"	"	<0.5	5	130
10	"	"	<0.5	5	60
11	"	"	<0.5	5	100
12	"	"	<0.5	16	450
13	"	"	<0.5	2.5	<15
14	"	"	<0.5	14	480
15	"	"	<0.5	5	235
16	"	Unknown	0.5	2	<15
17	"	"	0.5	2	25
18	"	"	<0.5	4	20
19	"	"	<0.5	4.5	125
20	"	"	<0.5	4	240
21	"	"	<0.5	2	100
22	"	"	<0.5	2.5	140
23	"	"	<0.5	4	15
24	"	"	<0.5	1.5	<15
25	"	"	<0.5	2.5	270
26	"	"	<0.5	4	50
27	"	"	<0.5	2.5	45
28	"	"	<0.5	5	140
29	Powder	"	0.5	5	45
30	"	"	<0.5	3.5	80
31	"	"	<0.5	8	145

TABLE VIII
HEAVY METAL CONTENT OF GELATIN AND IRISH MOSS GELOSE

Sample	Origin	As, p.p.m.	Pb, p.p.m.	Zn, p.p.m.	Cu, p.p.m.
Gelatin					
1	Canada	<0.5	5	<15	<10
2	"	<0.5	3	<15	<10
3	"	<0.5	6	<15	<10
4	"	<0.5	5	<15	<10
5	"	<0.5	1	<15	<10
6	New Zealand	1.5	1	90	<10
7	"	1.5	2	125	<10
8	"	1.5	1	70	<10
9	"	0.5	8	65	<10
10	Unknown	0.5	1	<15	<10
11	"	0.5	2	<15	<10
12	"	0.5	2	<15	<10
Irish moss					
1	U.S.A.	0.5	2	75	<10
2	"	0.5	3	<15	<10
3	"	1	15	<15	30
4	"	0.5	3.5	<15	30
5	"	0.5	6	<15	20

Irish Moss Gelose (Carrageen)

Although carrageen is used extensively in the food industry, much of it is imported into Canada in stabilizing mixtures. The results on available samples are given in Table VIII. Only one sample contained more than 50 p.p.m. of zinc and one contained 15 p.p.m. of lead. Copper seems to occur in carrageen to a greater extent than in the other gelling agents.

Miscellaneous

The heavy metal content of single samples of miscellaneous stabilizing agents is given in Table IX. One sample of locust bean gum (carob gum) contained 6.1 p.p.m. of arsenic which was the highest arsenic recorded in the sur-

TABLE IX
HEAVY METAL CONTENT OF MISCELLANEOUS GELLING AND
STABILIZING AGENTS

	As, p.p.m.	Pb, p.p.m.	Zn, p.p.m.	Cu, p.p.m.
Sodium pectate	1	6	130	10
Liquid pectin	1.3	1.1	<10	<10
Karaya gum	<0.5	1.3	30	<10
Gum arabic	<0.5	1.7	<10	<10
Locust bean gum	2.0	0.9	27	<10
Locust bean gum	6.1	3.2	22	<10
Sodium carboxy-methylcellulose	<0.5	1.7	10	<10
Methylcellulose	<0.5	0.9	<10	<10
Stabilizing mixture ¹	1.4	25	50	<10
Stabilizing mixture ¹	<0.5	2.2	54	<10
Sodium alginate	0.5	4	20	<10
Sodium alginate	0.5	38	15	<10
Algin	1.5	3.5	<15	<10

¹The composition of the mixtures was stated to be agar, dextrose, carob, and karaya.

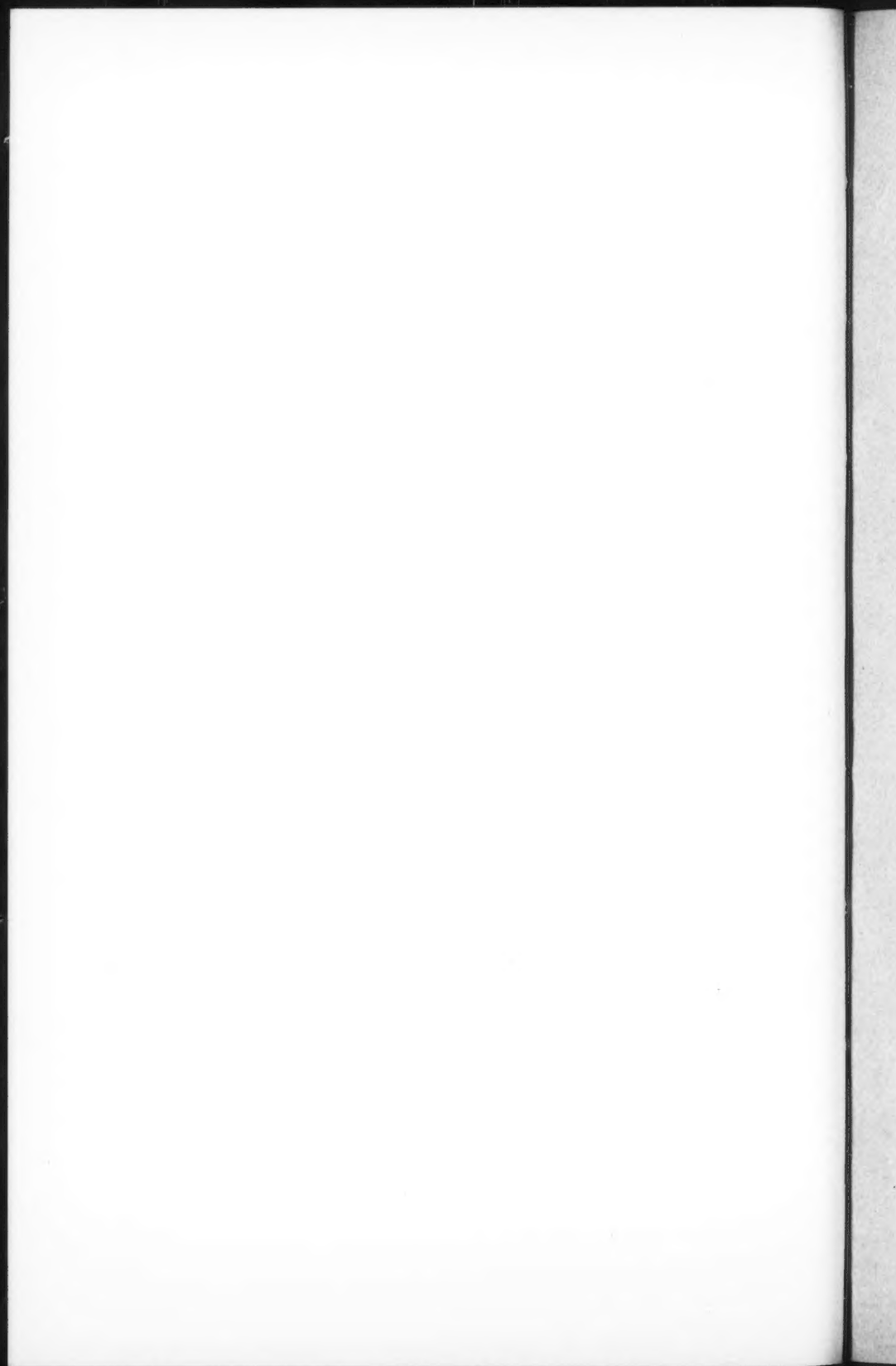
vey. The mixtures examined were stated to consist of agar, dextrose, carob, and karaya. The reason for the high lead content of one of the samples is not evident, since the normal lead content of the constituents is low. The lead content of 38 p.p.m. of one of the samples of sodium alginate is excessive and would render the product unsuitable for use in foods.

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